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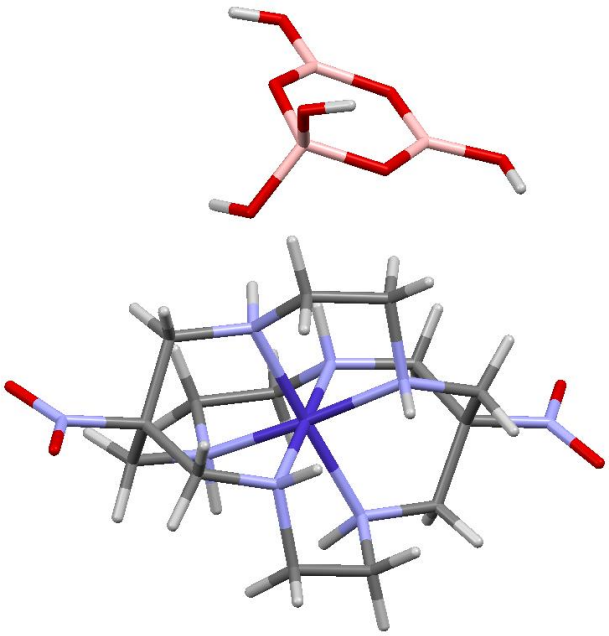
Polyborate anions templated by cationic transition-metal complexes: $[Co(diNOsar)]_2[B_3O_3(OH)_4]Cl_5{\cdot}4.75\ H_2O$

Mohammed A. Altahan[1], Michael A. Beckett[1*], Simon J. Coles[2], Peter N. Horton[2]

[1]*School of Chemistry, Bangor University, Bangor, Gwynedd, LL57 2UW, UK*

[2]*School of Chemistry, Southampton University, Southampton, SO17 1BG, UK*

GRAPHICAL ABSTRACT



Abstract *The transition metal complexes $[Co(diNOsar)]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(dien)_2]^{3+}$ have been used to template unusual isolated polyborate anions by reaction of basic aqueous solutions containing the cations with $B(OH)_3$ (1:10). The synthesis and characterization (TGA/DSC, IR, NMR, single-crystal XRD) of one such complex $[Co(diNOsar)]_2[B_3O_3(OH)_4]Cl_5.4.75H_2O$ (**1**) is reported. Compound **1** is a rare example of a salt containing the isolated triborate(1-) anion, and its formation is engineered by the cation, which has extensive H-bond interactions with the anion in its secondary coordination sphere.*

Keywords Triborate(1-); Self-assembly; H-bonds; $[Co(diNOsar)]^{3+}$; X-ray Structure; Oxidoborate

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Address correspondence to Dr M.A. Beckett, School of Chemistry, Bangor University, Bangor, Gwynedd, UK.
Email: m.a.beckett@bangor.ac.uk
Electronic supplementary information (ESI) available. CCDC 1423520. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

INTRODUCTION

Polyborate anions are conveniently classified[1] as either polymeric (2D or 3D chains, sheets or networks) or discrete 'isolated' anionic moieties. Isolated polyborate anions are readily synthesized by the addition of $B(OH)_3$ to a basic aqueous solution containing templating cations[2], or by solvothermic[3] methods. Templated products arise since $B(OH)_3$ in basic aqueous solution exists as a dynamic combinatorial library of polyborate anions[4]. In general, pentaborate(1-) salts (containing the $[B_5O_6(OH)_4]^-$ anion) are formed because these salts have a strong H-bonded anionic lattice, which is sufficiently flexible to accommodate many medium sized cations[5]. Salts containing polyborate anions other than pentaborate(1-) are relatively rare[6]. We are interested in the synthesis of structurally novel polyborate anions and have adopted a strategy of templating such species by the use of sterically demanding and/or highly charged cations[7,8]. Herein, we report the synthesis of several salts containing isolated polyborate anions partnered with transition metal cations and describe in detail the synthesis and characterization of the salt $[Co(diNOsar)]_2[B_3O_3(OH)_4]Cl_5{\cdot}4.75\,H_2O$ (**1**) which contains the isolated triborate(1-) anion.

RESULTS AND DISCUSSION

Synthesis

Halide salts of transition-metal complexes are readily transformed, provided they are stable in basic solution, into their hydroxide salts by use of a Dowex 550A hydroxide activated anion exchange resin. The resulting aqueous solutions, which are separated from the resin, were reacted with $MeOH/H_2O$ solutions of $B(OH)_3$ (1:10) to afford polyborate anions salts of cationic transition-metal complexes. Several salts have been prepared *e.g.* $[Co(diNOsar)]_2[B_3O_3(OH)_4]Cl_5{\cdot}4.75H_2O$ (**1**), $[Co(en)_3][B_5O_6(OH)_4][B_8O_{10}(OH)_6]{\cdot}5H_2O$ (**2**), *s-fac*-$[Co(dien)_2][B_7O_9(OH)_6]{\cdot}9H_2O$ (**3**). Compounds **2** and **3**, which contain previously unobserved octaborate(2-) and heptaborate(3-) anions, were prepared in reasonable yields (~40%) and details[7,8] of their synthesis and full characterization can be found elsewhere. The starting complex $[Co(diNOsar)]Cl_3$ was prepared by a reported[9] procedure for the synthesis of **1**. Compound **1** was isolated in low yield (10%) and its high chloride content would indicate that

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the ion exchange was not completely successful in this case. Nevertheless, we were able to characterize[10] the compound by elemental analysis, mpt, thermally (TGA/DSC) and by NMR (^{1}H, ^{13}C, ^{11}B) and IR spectroscopy. Single-crystals were also suitable for a XRD study.

NMR spectra of **1** were obtained in D_2O. The ^{1}H NMR spectrum of **1** consists of AB doublets for the CH_2 groups of the capping units and a complex AA'BB' pattern[11] (looking like a doublet with J = 9.2 Hz) for the CH_2 protons of the ethylenediamine rings. The secondary amine protons are observed with the residual HOD signal at δ = 4.70 ppm. The $^{13}C\{^{1}H\}$ spectrum shows the expected 3 signals at δ = 51.4 (ethylene diamine groups), δ = 55.1 (CH_2 of capping groups) and δ = 87.8 ppm (tertiary C-NO_2 cap). As a consequence of boron exchange associated with rapid $B(OH)_3/[B(OH)_4]^-$/polyborate equilibria[4] the ^{11}B spectrum shows just one signal at δ = +16.2 ppm.

Thermal (TGA) analysis in air was consistent with a three step process involving low temperature (<125 ^{o}C) loss of water of crystallization, further dehydration to form an anhydrous polyborate (200-275 ^{o}C), and oxidation of organics (275-800 ^{o}C) to leave a glassy inorganic residue of composition $Co_2B_3O_5Cl_5$. Such thermal decomposition has been previously observed[12] for transition-metal polyborate salts.

X-ray structure of $[Co(diNOsar)]_2[B_3O_3(OH)_4]Cl_5 \cdot 4.75H_2O$

Full crystallographic data for **1** are available in the supplementary information[13] and crystallographic data are summarized in a footnote[14]. Compound **1** is an ionic compound and is a rare example of a salt containing the triborate(1-) anion. In addition to the $[B_3O_3(OH)_4]^-$ anion, **1** contains 2 independent $[Co(diNOsar)]^{3+}$ cations, 5 Cl^- anions and 4.75 H_2O molecules. There is a disordered water within the asymmetric unit. One area can exist as either one (25%) or two (75%) molecules of water, hence the fractional formula. Atomic labelling for the triborate(1-) anion is shown in Figure 1.

The $[Co(diNOsar)]^{3+}$ cation comprises a central Co^{3+} ion surrounded by the 6 N donor atoms of the hexadentate neutral 'diNOsar' ligand in a distorted octahedral environment. *Cis* and *trans* N-Co-N angles range from 86.43(9) - 92.58(9)^{o} (av. 90.06^{o}) and 175.79(9) - 178.12(10)^{o}

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(av. 176.62°) respectively. The Co-N bond lengths range from 1.963(2) - 1.975(2) Å, av. 1.969 Å. These data are not significantly different from previously reported data[15] for this cation.

The $[B_3O_3(OH)_4]^-$ ion of **1** possesses a B_3O_3 (boroxole) ring with one 4-coordinate and two 3-coordinate B centres. B-O bond lengths to 3-coordinate (B2 and B3) and 4-coordinate (B1) B centres range from 1.347(4) - 1.386(4) Å (av. 1.363 Å) and 1.466(4) - 1.471(4) Å (av. 1.488 Å), respectively. B2-O1 (1.351(3) Å) and B3-O3 (1.347(4) Å) are significantly shorter than the other B-O bonds within the boroxole rings. The boroxole ring is planar with ring angles ranging from 112.3(2) – 122.4(2)°. The smallest ring angle (O1B1O3) involves the 4-coordinate B centre, whereas ring angles at O1, O2, and O3 average 121.1° and those at the 3- coordinate B centres (B2 and B3) average 121.6°. This pattern of bond angles and bond lengths are in accord with previously reported data for this anion[16] and mirror corresponding data observed[17] in related isoelectronic systems such as $Ar_3B_3O_3{\cdot}L$ and $[Ph_3B_3O_3{\cdot}(OH)]^-$.

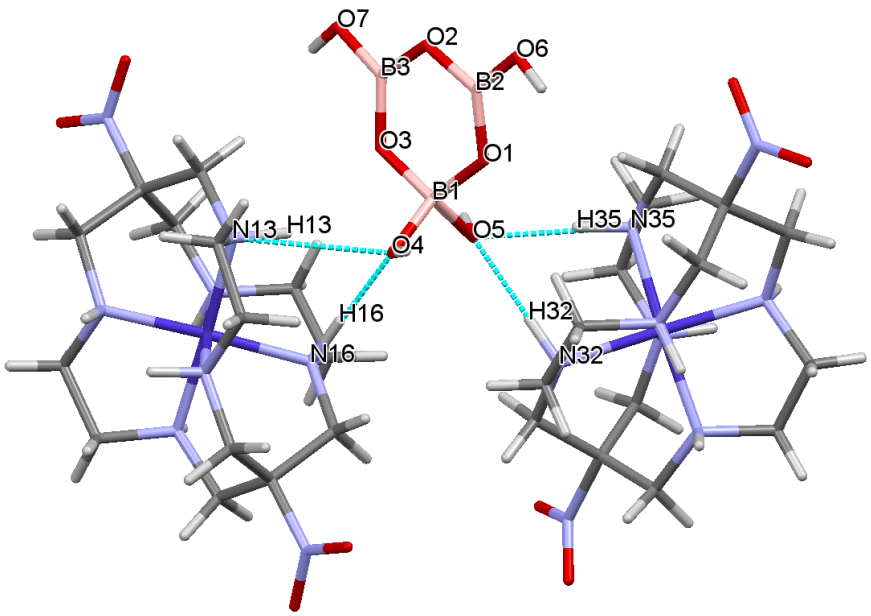

Figure 1 Cation-triborate H-bond interactions in **1**. *d*(N13-H13) 1.00 Å, *d*(H13···O4) 1.98 Å, *d*(N13···O4) 2.935(3) Å, <(N13H13O4) 159.2°; *d*(N16-H16) 1.00 Å, *d*(H16···O4) 1.73 Å, *d*(N16···O4) 2.731(3) Å, <(N16H16O4) 177.4°; *d*(N32H32) 1.00 Å, *d*(H32···O5) 1.81 Å, *d*(N32···O5) 2.810(3) Å, < (N32H32O5) 175.8°; *d*(N35-H35) 1.00 Å, *d*(H35···O5) 1.93 Å, *d*(N35···O5) 1.93 Å, *d*(N35···O5) 2.898(3) Å, <(N35H35O5) 163.4°.

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There are multiple H-bond interactions within the solid-state structure of **1**. Full details can be found in the supplementary information. Polyborate anions usually display multiple anion-anion H-bond interactions and these are believed[5] to be the driving force in the synthesis of non-metal cation pentaborate(1-) salts. Anion-anion interactions were found to be present in **2** and **3**. However, in **1**, triborate-triborate H-bond interactions are absent and each triborate(1-) anion is isolated from others by H_2O bridges, forming a sheet-like structure (Figure 2). This isolation implies that the crystal structure of **1** is engineered by interactions with other components within the system. The triborate(1-) anion is able to form 4 donor H-bonds and has 7 potential H-bond acceptor sites. The triborate(1-) anion in **1** does indeed form 4 donor interactions: three to H_2O molecules and one to a Cl^- anion (O6H6···Cl2). The triborate(1-) anion accepts 2 H-bonds at each hydroxyl group (O4 and O5) on the 4-coordinate B1, and also at O6 from H_2O (O54-H54···O6). The H-bonds directed at O4 and O5 originate from amine hydrogens on two $[Co(diNOsar)]^{3+}$ cations in a chelating mode, as illustrated in Figure 1. These H-bond interactions are likely to be responsible for templating this salt and assembling the triborate(1-) anion. Secondary amine hydrogens of $[Co(diNOsar]^{3+}$ are known[15] to form similar H-bond interactions *e.g.* $[Co(diNOsar)][S_2CN(CH_2)_4]_3$.

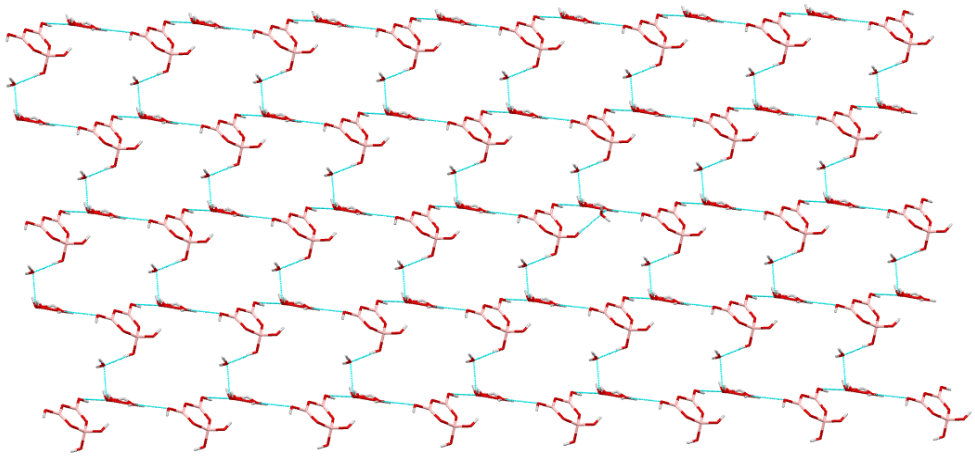

Figure 2 The triborate(1-) anions are arranged in planes linked together by H-bonds from H_2O molecules. The $[Co(diNOsar)]^{3+}$ cations fill the cavities and H-bond to the triborate(1-) anions.

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Summary

$[Co(diNOsar)]_2[B_3O_3(OH)_4]Cl_5.4.75H_2O$ is a rare example of a salt containing the isolated triborate(1-) anion. It has been obtained from a self-assembly reaction of (partially) OH^- exchanged aqueous solution of $[Co(diNOsar)]Cl_3$ with $B(OH)_3$ (1:10). The solid-state structure of **1** shows the anion in the secondary coordination sphere of the cation. There are strong cation-anion H-bond interactions, which help to engineer the formation of the triborate(1-) anion.

REFERENCES

1. (a) Christ, C.L.; Clarke, J.R. *Phys Chem. Miner*, **1977**, 2, 59-87; (b) Schubert, D.M.; Smith, R.A.; Visi, M.Z. *Glass Technol.* **2003**, 44, 63-70.
2. Beckett, M.A.; Horton, P.N.; Coles, S.J.; Martin, D.W. *Inorg. Chem*., **2011**, 50, 12215-12218.
3. (a) Wang, G.-M.; Pan, C.-Y.; Zheng, S.-T.; Yang, G.-Y. *Acta Cryst*. **2007**, E63, o1104-o1105; (b) Wang, G.-M.; Sun Y.-Q.; Yang, G.-Y. J. Solid State Chem. **2004**, 177, 4648-4654.
4. (a) Salentine, C.G. *Inorg. Chem*. **1983**, 22, 3920-3924; (b) Anderson, J.L.; Eyring, E.M.; Whittaker, M.P. *J. Phys. Chem.* **1964**, 68, 1128-1132.
5. Beckett, M.A.; Coles, S.J.; Davies, R.A.; Horton, P.N.; Jones, C.L. *Dalton Trans.* **2015**, 44, 7032-7040.
6. Schubert, D.M.; Knobler, C.B. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* **2009**, 50, 71-78.
7. Altahan, M.A.; Beckett, M.A.; Coles, S.J.; Horton, P.N. *Inorg. Chem.* **2015**, 54, 412-414.
8. Altahan, M.A.; Beckett, M.A.; Coles, S.J.; Horton, P.N. *Inorg. Chem. Commun.* **2015**, 59, 95-98.
9. Geue, R.J.; Hambley, T.W.; Harrowfield, J.M.; Sargeson, A.M.; Snow, M.R. *J. Am. Chem. Soc.* **1984**, 106, 5478-5488.
10. Characterization data for **1**: $C_{28}H_{73.50}B_3Cl_5Co_2N_{16}O_{19.75}$. Elem. Anal Calc: C, 26.3; H 5.8; N, 17.5. Found: C, 25.6; H 6.5; N, 16.7%. Mp 285 ^oC. TGA: - 4.75 H_2O 7.8 % (6.7 % calc.), - $2H_2O$ 3.2 % (2.8% calc.), cation oxidation 57.7 % (58.6% calc.), residual $Co_2B_3O_3Cl_5$ 31.3% (31.9 % calc). IR (KBr/cm^{-1}): 3401(br,s), 3041(vs), 2871(vs), 1558(vs), 1432(m), 1345(s), 1077(m), 988(w), 849(w), 813(w). NMR (400 MHz, D_2O) δ^1H/ppm: 3.77 6H (d, 13.8 Hz), 3.41 6H (m), 3.24 6H (d, 13.8 Hz), 2.83 6H (m). $\delta^{11}B$/ppm: 16.2. $\delta^{13}C$/ppm: 87.8, 55.1, 51.4.
11. Bernhardt, P.V.; Bygott, A.M.T.; Geue, R.J.; Hendrey, A.J.; Korybut-Daszkiewicz, B.R.; Lay, P.A.; Pladziewicz, J.R.; Sargeson, A.M.; Willis, A.C. *Inorg. Chem.* **1994**, 33, 4553-4561.
12. (a) Wang, G.-M.; Sun, Y.-Q.; Yang, G.-Y. *J. Solid State Chem.* **2006**, 179, 1545-1553; (b) Liu, Z.-H.; Zhang, J.-J.; Zhang, W.-J. *Inorg. Chim. Acta* **2006**, 359, 519-524; (c) Yang, Y.; Wang, Y.; Zhu, J.; Liu, R.-B.; Xu, J.;

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Meng, C.-C. *Inorg. Chim. Acta* **2011**, 376, 401-407; (d) You, X.; Zhu, L.; Sun, J. *Chin. J. Chem.* **2010**, 28, 2174-2178.

13. (a) Coles, S.J.; Gale, P.A. *Chem. Sci.* **2012**, 3, 683-689; (b) Rigaku, CrystalClear-SM Expert 3.1 **2013**, b27; (c) Sheldrick, G.M. *Acta Crystallogr*. **2015**, C71, 3; (d) Farrugia, L.J.; *J. Appl. Crystallogr*. **1997**, 30, 564; (e) Palatinus, L.; Chapuis, G.; *J. Appl. Crystallogr*. **2007,** 40, 786-790; (f) CrysAlisPro, Agilent Technologies, version **2014**, 1.171.37.31.
14. A *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of a *FR-E+ SuperBright* molybdenum rotating anode generator with VHF *Varimax* optics (70μm focus) was used. X-ray data for **1**: $C_{28}H_{73.50}B_3Cl_5Co_2N_{16}O_{19.75}$, M = 1278.06; triclinic space group *P*-1, *a* = 9.6900(4) Å, *b* = 10.0170(6) Å, *c* = 29.1374(7) Å, α = 85.079(3)°, β = 88.439(3)°, γ = 62.137(5)°; *U* = 2490.9(2) $Å^3$; *Z* = 2; *T* = 100K; Wavelength = 0.71075 Å; density (calc) = 1.704 Mg/m^3; Absorption coefficient 1.024 mm^{-1}; Crystal: orange lath, 0.180 x 0.030 x0.010 mm^3; *F(000)* 1331; θ range for data collection 2.420-29.944°; Index ranges $-13 \le h \le 12$, $-13 \le k \le 13$, $-38 \le l \le 40$; 36914 reflections collected with 12826 independent reflections [R_{int} = 0.0478]; Completeness to θ = 25.242°, 99.9%; absorption correction: semi-empirical from equivalents; refinement method: full-matrix least squares on F^2; data/restraints/parameters 12826/0/668; goodness-of-fit on F^2, 1.023; Final *R* indices [$F^2 > 2\sigma(F^2)$] *R1* = 0.0485, *wR2* = 0.0976; *R* indices (all data) *R1* = 0.0740, *wR2* = 0.1072; extinction coefficient n/a; largest diff. peak and hole 0.881 and -0.662 e $Å^{-3}$.
15. Achilleos, A.A.; Gahan, L.R.; Hambley, T.W.; Healy, P.C.; Weedon, D.M. *Inorg. Chim. Acta* **1989**, 157, 209-214.
16. (a) Negro, A.D.; Pozaz, J.M.M.; Ungaretti, L. *Am. Mineral* **1975**, 60, 897-883; (b) Salentine, G.C.; *Inorg. Chem.* **1987**, 26, 128-132; (c) Beckett, M.A.; Horton, P.N.; Hursthouse, M.B.; Timmis, J.L. *RSC Adv.* **2013**, 3, 15185-15191; (d) Schubert, D.M.; Visi, M.Z.; Knobler, C.B. *Inorg. Chem*. **2008**, 47, 2017-2023.
17. (a) Beckett, M.A.; Coles, S.J.; Light, M.E.; Fischer, L.; Stiefvater-Thomas, B.M.; Varma, K.S. *Polyhedron* **2006**, 25, 1011-1016; Beckett, M.A.; Hibbs, D.E.; Hursthouse, M.B.; Owen, P.; Malik, K.M.A.; Varma, K.S. *Main Group Chem*. **1998**, 2, 251-258; (c) Beckett, M.A.; Strickland, G.C.; Varma, K.S.; Hibbs, D.E.; Hursthouse, M.B.; Malik, K.M.A. *J. Organomet. Chem*. **1997**, 535, 33-41.

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